



# Impact of cation selection on proton exchange membrane fuel cell performance with trimethylethyl amide, ethylpyridinium and ethylmethyl imidazolium ionic liquid carried by poly(vinylidene fluoride) membrane as electrolyte



Jian Gao <sup>a,b</sup>, Yong Guo <sup>c</sup>, Bingbing Wu <sup>a</sup>, Li Qi <sup>a</sup>, Bo Li <sup>a</sup>, Jianguo Liu <sup>a,\*</sup>, Zhongwei Wang <sup>a</sup>, Wenming Liu <sup>a</sup>, Jun Gu <sup>a</sup>, Zhigang Zou <sup>a,\*\*</sup>

<sup>a</sup> Eco-materials and Renewable Energy Research Center, Department of Materials Science and Engineering, National Laboratory of Solid State Microstructures, Nanjing University, 22# Hankou Road, Nanjing 210093, China

<sup>b</sup> Department of Chemical Engineering, Tianjin Polytechnic University, 399# Binshui West Road, Tianjin, China

<sup>c</sup> State Key Laboratory of Pollution Control & Resource Reuse, School of the Environment, Nanjing University, 22# Hankou Road, Nanjing, China

## HIGHLIGHTS

- Impact of cation selection on PEM fuel cell performance was studied.
- The results shed more light on the influence of organic cations on the Pt/C catalyst.
- The results show that the influence of ILs on the Pt/C should be considered.
- The work provides helpful information in applying ILs as electrolyte for PEMFC.

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## ABSTRACT

The cation impact of trimethylethyl amide ( $[N1114]^+$ ), ethyl pyridinium ( $[Epdy]$ ) and ethylmethyl imidazolium ( $[Emim]^+$ ) on the performance of proton exchange membrane fuel cell (PEMFC) is studied. The cell performance with ionic liquid (IL) as the electrolyte is dramatically improved by replacing  $[Emim]$  cation with  $[N1114]$ . A maximum power density (MPD) of  $65 \text{ mW cm}^{-2}$  is obtained with  $[N1114]HSO_4$  as the electrolyte in PEMFC while the one with imidazolium ILs can only provide around  $1 \text{ mW cm}^{-2}$ . Subsequently, the influence of cations of ILs on Pt/C catalyst is investigated by cyclic voltammogram, and it can be found that the imidazolium cation result in smaller electrochemical active surface areas (EAS) of Pt/C than those of  $[N1114]^+$  and pyridinium. In addition, theoretical calculation with the Gaussian 03 program implies that the adsorption energy of the  $[Emim]^+$  on the Pt catalyst surface is much higher than  $[N1114]^+$ , thus decreasing EAS of Pt catalyst in fuel cells. Therefore, it indicates that the cation should be carefully selected when applying ILs as an electrolyte for fuel cells.

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## 1. Introduction

Ionic liquids (ILs) are usually defined as salts with a melting point below  $100^\circ\text{C}$  [1–3]. ILs are a subject of current interest in various research circles for their unique properties such as good thermal and electrochemical stability, low vapor pressure, high ionic conductivity, and low melting points [4–7]. Recently, ILs have

been proposed as electrolytes in place of state-of-the-art electrolyte of Nafion membranes for the proton exchange membrane fuel cell (PEMFC) [8–16], which has been considered as an efficient and clean power source alternative to the conventional ones [17,18]. The ILs are proposed as a potential alternative electrolyte mainly because of their high ionic conductivity independent of liquid water, so as to simplify the humidifying structures in fuel cell system [8,11,19]. Additionally, the high price of Nafion membrane necessitates alternative electrolyte for PEMFC [20–24].

Until now, imidazolium salts have been the most investigated ILs. However, most of the fuel cells with these ILs as electrolyte can only provide rather low fuel cell performance, and the maximum power

\* Corresponding author. Tel.: +86 25 83621219; fax: +86 25 83686632.

\*\* Corresponding author. Tel.: +86 25 83686630; fax: +86 25 83686632.

E-mail addresses: [jianguoliu@nju.edu.cn](mailto:jianguoliu@nju.edu.cn), [jgliu2005@googlemail.com](mailto:jgliu2005@googlemail.com) (J. Liu), [zgou@nju.edu.cn](mailto:zgou@nju.edu.cn) (Z. Zou).

density (MPD) averages around  $1 \text{ mW cm}^{-2}$  [25–27]. The poor performance has been attributed to several causes such as the test station [26], unfavourable fuel cell structure [27], and low conductivity of the membrane-IL composite [28]. However, little attention was paid to the influence of ILs themselves. In the PEMFCs with IL as electrolyte, the IL has to be loaded in a porous matrix before working as the electrolyte in the fuel cell. The binding in the composite membrane between IL and the porous matrix is mainly due to Van der Waals forces instead of strong chemical bonding. As a result, the leaching of ILs from the matrix is unavoidable. The leached IL inside the composite membrane will move to the catalyst and possibly influence the catalyst activity. Therefore, the possible effect from the ILs on the fuel cell catalyst should be investigated. Our group has investigated the effect of halide impurities in the imidazolium ILs and obvious negative effects of  $\text{Br}^-$  were observed [29]. However, no obvious improvement in the PEMFC performance was obtained even with halide free imidazolium ILs [25]. Further investigation shows that the imidazolium ILs depress the electrochemical active surface area (EAS) of the Pt/C catalyst. Therefore, it is reasonable to speculate that the imidazolium cation may be another factor causing the poor performance, and ILs with other cations may be found to elevate the performance of PEMFC with ILs as electrolyte.

This work aims to investigate the impact of cations of the ILs on the PEM fuel cell performance. The results show that the PEMFC with non-imidazolium ILs can provide elevated performance. Especially, the PEMFC with quaternary IL of trimethylethyl amide hydrosulphate ( $[\text{N}1114]\text{HSO}_4$ ) can work with MPD of  $65 \text{ mW cm}^{-2}$ . This value is around 60 times that of the fuel cell with imidazolium IL as electrolyte. Electrochemical methods were applied to study the mechanism for the performance elevation. To further investigate the mechanism for the performance increase, density functional theory calculations were carried out to obtain the adsorption energy of the cation on the Pt catalyst, and which are consistent with the cyclic voltammogram and fuel cell test results.

## 2. Experimental section

### 2.1. Synthesis of ILs

#### 2.1.1. Ethylmethyl imidazolium hydrosulphate ( $[\text{Emim}]\text{HSO}_4$ )

This IL was prepared with the method described in the previous work [29]. Briefly,  $\text{N}$ -methylimidazole was firstly reacted with diethyl sulphate to obtain  $[\text{Emim}]\text{EtOSO}_3$ . The  $[\text{Emim}]\text{EtOSO}_3$  was subsequently reacted with KOH in ethanol solution to prepare  $[\text{Emim}]\text{OH}$  solution.  $\text{H}_2\text{SO}_4$  was then added to the obtained  $[\text{Emim}]\text{OH}$  solution to prepare  $[\text{Emim}]\text{HSO}_4$ .

#### 2.1.2. Trimethylethyl amide hydrosulphate ( $[\text{N}1114]\text{HSO}_4$ )

This IL was prepared via our previously reported method with some adjustment [29]. A 0.03 mol dibutyl sulphate ( $\text{Bu}_2\text{SO}_4$ ) was added in drop-by-drop to 0.03 mol trimethylamine solution in water (33% wt) while stirring in water bath of room temperature. The system was observed to increase in temperature and decrease in pressure. These phenomena were expected as a result of the reaction of volatile  $\text{N}(\text{CH}_3)_3$  with  $\text{Bu}_2\text{SO}_4$ . After stirring for another 3 h, most of the water was removed on a rotary evaporator and a white solid was obtained ( $[\text{N}1114]\text{BuOSO}_3$ ). 50 ml ethanol was added to the solid and a solution was obtained. The solution was added to 0.045 mol KOH dissolved in 100 ml ethanol. The filtrate was collected and the ethanol was removed on the rotary evaporator to obtain a viscous liquid, which transformed slowly to a white solid at room temperature. The melting point of the white solid was measured to be 30–40 °C and can remain as a super-cold liquid for several hours at 25 °C. This salt can be dissolved in ethanol and water, but not in acetone.

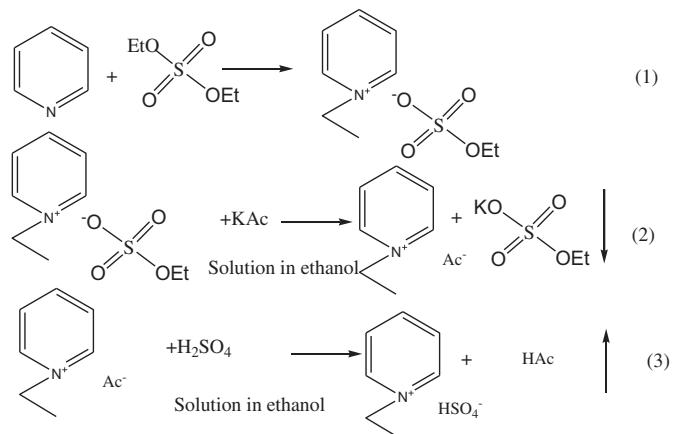


Fig. 1. Synthesizing process of  $[\text{Epdy}]\text{HSO}_4$ .

#### 2.1.3. Ethyl pyridinium hydrosulphate ( $[\text{Epdy}]\text{HSO}_4$ )

This IL was prepared via the process shown in Fig. 1. It is similar with our previously reported method [29] but with an important adjustment by replacing the KOH with  $\text{CH}_3\text{COOK}$  (KAc). The KOH used in the previous work must be replaced with some other K-containing salts that can be dissolved in ethanol as “ $[\text{Epdy}]\text{OH}$ ” cannot exist stably even in solution [30]. As a result, we selected KAc to replace KOH as the former has a high solubility in ethanol but much lower alkalinity. In this process, a 0.3 mol diethyl sulphate was added drop-by-drop to 0.3 mol pyridine while keep stirring in a water bath of room temperature. The system temperature was observed to reach around 50 °C during this process. The mixture was then stirred 24 h in a water bath of 50 °C. The resultant viscous liquid was added to 0.45 mol KAc dissolved in 300 ml ethanol drop-by-drop, and a white precipitate was generated. The system was stirred 3 h and then the precipitate was filtered and the filtrate was collected. Subsequently, 0.45 mol  $\text{H}_2\text{SO}_4$  dissolved in ethanol was added into the above filtrate. A white precipitate was generated and filtered. The filtrate was put in a rotary evaporator to remove most of the ethanol and HAc, and a crude product was obtained. The product was then washed with 20 ml ether for three times. The resultant liquid was then dried at 60 °C in atmosphere and vacuum subsequently to obtain the final product. The structure of the cation was confirmed with  $^1\text{H}$ NMR (see Supplementary data).

### 2.2. Single cell test

The IL was carried in a porous membrane to function as an electrolyte. In this study, a 45 mm × 45 mm (with thickness of 200  $\mu\text{m}$ ) sized membrane of PVDF with a pore diameter of 0.45  $\mu\text{m}$  was chosen as a carrier for its high chemical and electrochemical stability. The high viscosity of the IL makes it difficult to enter the microspores of the membrane. Therefore, the prepared IL was firstly dissolved in ethanol to obtain a solution (50% wt) of low viscosity. The ethanol was selected since it can dissolve the IL and can be removed from the IL easily by heating. The membrane was then immersed in the IL solution for 24 h at room temperature. The wet membrane was then dried at 60 °C for 24 h to vaporize the ethanol, leaving pure IL in the membrane.

The membrane was then sandwiched between two pieces of catalysed carbon paper to prepare a membrane electrode assembly (MEA). The Pt/C catalyst loading was  $0.4 \text{ mg cm}^{-2}$ , and the area is  $2.5 \text{ cm} \times 2.5 \text{ cm}$ . The MEA was subsequently clamped between two graphite blocks with serpentine flow channels for hydrogen and oxygen flow and the cell was clamped between two stainless steel plates using a set of retaining bolts around the periphery of the cell.

PTFE sheets were used on both sides of the MEA for isolation and sealing. Electrical heaters with control systems were placed in each graphite block to heat the cell to the desired operating temperature. Hydrogen and oxygen were supplied at a flow rate of 10 and 20  $\text{mL min}^{-1}$ , respectively. Current and voltage were recorded with a multimeter (PLZ70UA Japan) at 50 °C.

Subsequently, the fuel cells with  $[\text{N}1114]\text{HSO}_4$  and  $[\text{Emim}]\text{HSO}_4$  were tested for stability at current densities of 40 and 10  $\text{mA cm}^{-2}$ , respectively. The fuel cell with  $[\text{N}1114]\text{HSO}_4$  was also tested with the temperature elevated to 70 °C. The fuel cell was stabilized at least 5 min at 70 °C before the test was conducted.

### 2.3. Electrochemical tests

The ionic conductivity of  $[\text{N}1114]\text{HSO}_4$  and  $[\text{Epdy}]\text{HSO}_4$  was measured with a conductivity meter (Orion Star and Plus meter) at 5 °C interval in the range of 25–85 °C.

Cyclic voltammogram (CV) tests were carried out with the method described in detail in the previous work and summarized here [29]. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For each IL, the Pt/C catalyst was characterised at a scan rate of 20  $\text{mV s}^{-1}$  with 10,000 ppm of the ILs. The supporting electrolyte for the electrochemical tests was  $\text{H}_2\text{SO}_4$  solution (0.5 mol  $\text{L}^{-1}$ ).

The working electrode was fabricated by casting Nafion impregnated Pt/C (Pt 60 wt%, Johnson Matthey, UK) catalyst ink onto a glass carbon disk electrode with a diameter of 0.5 cm. The catalyst loading was 0.15 mg Pt  $\text{cm}^{-2}$ . The tests were performed with the concentration of 10,000 ppm IL as the previous work shows that a concentration of 10,000 ppm is high enough to show effects, if any exist [23].

### 2.4. Theoretical calculation

All calculations were performed with B3LYP methods [31] in the Gaussian 03 program [32]. A Pt cluster model containing 13 Pt atoms (Pt13) was constructed to simulate the structure of Pt. Cluster model, which has been widely used to investigate the performance of Pt catalysts [33]. Since Pt is a good catalyst for hydrogen activation and investigate in acid condition, Pt should have an interaction with protons. Thus, a new model (Pt13-2H) containing Pt13 and two protons were further constructed to simulate the structure of Pt in acid condition. These cations of ILs with N atoms are also possible protonated in acid conditions. Full molecular models were applied for these cations of ILs. LanL2DZ basis set was used to for the Pt atom, and 6-31G(d) basis set was applied to the rest of the atoms [34]. Given that ions are involved, solvent effect has been considered in all optimizations by using a PCM model [35] with water as solvent. All molecular structures were constructed with the Gview program based on the optimized results.

## 3. Results and discussion

### 3.1. IL synthesis

With a huge family of ILs [36], it is important to select appropriate formulations to be investigated. Until now, dialkylimidazolium salts are mostly investigated in fuel cells and other fields [2,37]. Thus, it is important to investigate its application in PEMFC as electrolyte. The dialkylimidazolium of  $[\text{Emim}]^+$  was first investigated in this paper.

Quaternary amide ILs is another kind of frequently studied ILs. Additionally, preliminary calculation of various ILs shows that the quaternary ammonium salt has the least negative effect on the

performance of Pt/C catalyst among the common ILs. Thus, this kind of salt was selected for study. However, many quaternary amides are of high melting point [29,38]. To apply the ILs as an electrolyte, it is better to prepare ILs of low melting point to form liquid. Since the increase of asymmetry of cation can cause a decrease in the melting point [39], IL of trimethylbutyl amine ( $[\text{N}1114]\text{HSO}_4$ ) was selected and prepared for its low asymmetry of the cation. The tests show that the melting point of the salt is 30–40 °C. Thus, this salt can be used directly as a liquid electrolyte.

For comparison, another kind of common IL of ethyl pyridinium ( $[\text{Epdy}]^+$ ) cation was studied.  $\text{HSO}_4^-$  was selected as the anion since it has a structural proton and has been consider as a potential proton conductor [40].

### 3.2. Single cell test

The single cell test results are presented in Fig. 2. The fuel cell worked poorly when the imidazolium IL of  $[\text{Emim}]\text{HSO}_4$  was used as an electrolyte. The maximum current density was a mere 10  $\text{mA cm}^{-2}$  and the MPD was a mere 1.6  $\text{mW cm}^{-2}$ . This is consistent with the reported performance for fuel cells with imidazolium ILs as electrolyte, as listed in Table 1. Thus, the experiment here and the literature imply that the PEMFC with imidazolium ILs has rather poor performance.

When the IL was replaced with non-imidazolium IL of  $[\text{Epdy}]\text{HSO}_4$ , the current density increased to approximately 70  $\text{mA cm}^{-2}$  as showed in Fig. 2. The MPD increased to 15  $\text{mW cm}^{-2}$ , nearly 10 times that of single cell with  $[\text{Emim}]\text{HSO}_4$ . Also, when non-imidazolium IL of  $[\text{N}1114]\text{HSO}_4$  was applied, the current density drastically increased to around 175  $\text{mA cm}^{-2}$  and the MPD increased to 65  $\text{mW cm}^{-2}$ . Additionally, increase in the open circuit voltage was also observed. To the best of our knowledge, this performance is the highest one reported in the literature with IL as the electrolyte in fuel cell. The fuel cell performance increase can be attributed to the replacing of imidazolium cations with non-imidazolium cation of  $[\text{N}1114]^+$ , and it implies that the cation markedly influences the fuel cell performance.

Stability is an important factor for fuel cell. During polarization curve tests with  $[\text{N}1114]\text{HSO}_4$  and  $[\text{Epdy}]\text{HSO}_4$ , no significant decrease was observed. Therefore, it is reasonable to conclude that the fuel cell with  $[\text{N}1114]\text{HSO}_4$  and  $[\text{Epdy}]\text{HSO}_4$  can work for a relatively long term. However, continuous decrease of voltage was observed for IL with  $[\text{Emim}]\text{HSO}_4$ . Thus, the stability of fuel cell with  $[\text{Emim}]\text{HSO}_4$  can not be high. Therefore, fuel cells with  $[\text{N}1114]\text{HSO}_4$  and  $[\text{Emim}]\text{HSO}_4$  were selected and tested for stability at constant current discharging. The results are presented in Fig. 3. It

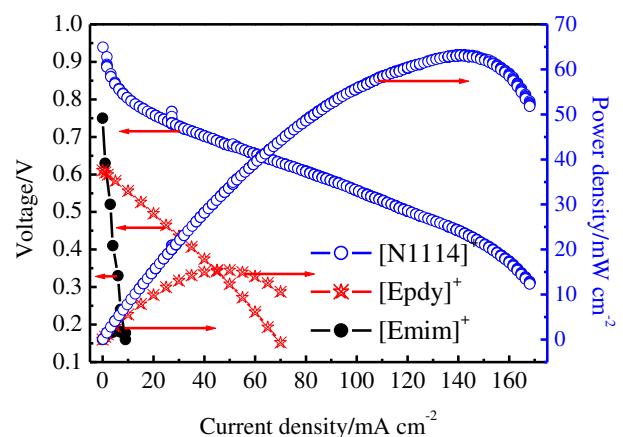


Fig. 2. Polarization curves of fuel cells at 50 °C.

**Table 1**

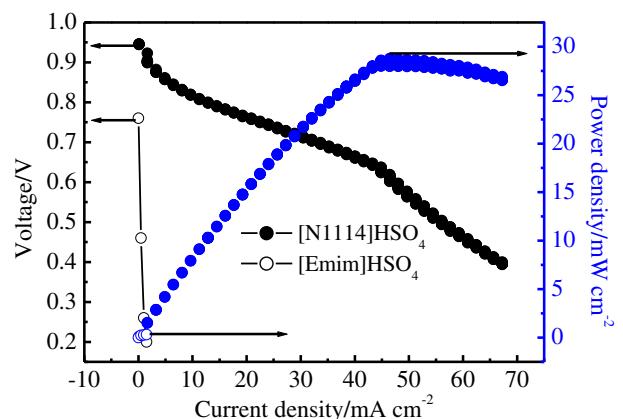
Typical fuel cell performance based on ionic liquids in the literature.

Entry	Cation	Anion	Carrier	OCVPt1/V	MPD/mW cm <sup>-2</sup>	Ref.
1	fx1	fx7	/	~0.78	~0.3	[13]
2	fx2	fx8	/	~0.9	0.6	[14]
3	fx3	fx9	PVDF–HEP	~0.45	~0.2	[26]
4	fx4	PF <sub>6</sub> <sup>-</sup>	PVdF–HFP	~0.75	<0.25	[27]
5	fx5	Cl <sup>-</sup> , BF <sub>4</sub> <sup>-</sup>	Polymeric membrane	0.8, 0.5	1.1; 1.2	[41]
6	fx6	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	PVDF–HEP	~0.6	~0.9	[42]

shows that the fuel cell with [N1114]HSO<sub>4</sub> can work at 40 mA cm<sup>-2</sup> with voltage higher than 0.65 V for nearly 1 h without significant decrease of performance. This means that the fuel cell can work even longer. However, the fuel cell with [Emim]HSO<sub>4</sub> can only “work” for around 30 s with a continuous decrease in performance. This performance decrease can not be simply attributed to the running out of the IL. Taking consideration of the CV tests in the following part, [Emim]HSO<sub>4</sub> have influenced the fuel cell performance mainly via an irreversible absorbing of cation on the catalyst.

Fuel cells with [N1114]HSO<sub>4</sub> and [Emim]HSO<sub>4</sub> were also tested with the temperature elevated to 70 °C, and the results are presented in Fig. 4. The MPD for fuel cell with [N1114]HSO<sub>4</sub> decreased to 29.2 mW cm<sup>-2</sup>, while fuel cell with [Emim]HSO<sub>4</sub> decreased to 0.2 mW cm<sup>-2</sup>. When the cell was disconnected after the cell test, a great part of the membrane in the upper side, around 80% percent of the area, was “dried” of the IL just by eyesight. This dry condition may largely be attributed to the decrease of viscosity with the elevation of cell temperature, leading to the aggregation of IL in the lower part of PVDF membrane by gravity. Since the dry PVDF itself can not work as electrolyte for PEMFC, the valid area of the fuel cell dramatically decreased. What is more, hydrogen or oxygen cross over through the membrane may take place via the porous in the dried area, causing the fuel cell performance decrease further. It should be mentioned that the fuel test at elevated temperature (70 °C) proves that the state-of-the-art PVDF membrane is not a suitable supporting material to hold ILs as electrolyte. Therefore, it is important to find a suitable carrier so as to development true “composite” with IL in PEM fuel cells in the follow-up development.

The results of single cell tests show that the fuel cell performance was elevated when imidazolium cations were replaced with the non-imidazolium one. Since the fuel cell tests were performed under the same conditions except for the cations, it is reasonable to attribute the fuel cell performance elevation to the replacement of the imidazolium cations but the reason for the performance

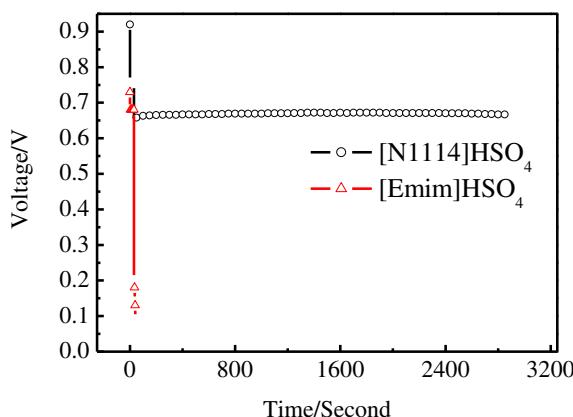
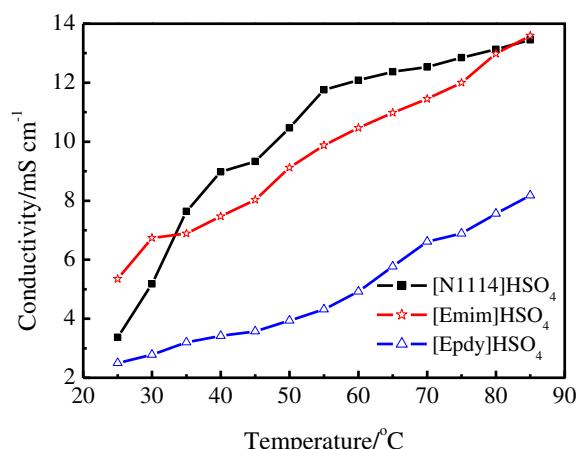
Fig. 4. Single cell test at 70 °C with [N1114]HSO<sub>4</sub> and [Emim]HSO<sub>4</sub> as electrolyte.

elevation remains unknown. As the fuel cell performance can be affected by the ionic conductivity of the electrolyte, we expected the fuel cell performance elevation may be a result of the elevation of the ionic conductivity for quaternary amid ILs. Therefore, the ionic conductivity of ILs was firstly measured at various temperatures.

### 3.3. Electrochemical tests

#### 3.3.1. Ionic conductivity

The ionic conductivity of the three ILs was investigated to see if the performance difference can be attributed to the conductivity. As presented in Fig. 5, the conductivity is in the range of 1–14 mS cm<sup>-1</sup>. This is consistent with the reported value [10,19,26,43], which is lower than that of Nafion operating in a well-humidified condition. However, even with the relatively low ionic conductivity, the fuel cell performance should not be that low since the conductivity has been considered to be acceptable [27,44]. Thus, the ionic conductivity can not explain the extremely low performance of PEMFC with ILs as electrolyte. Fig. 5 also shows that no significant difference exists in ionic conductivity between [N1114]HSO<sub>4</sub> and [Emim]HSO<sub>4</sub>. The conductivity for [Epdy]HSO<sub>4</sub> was observed to be 1–8 mS cm<sup>-1</sup>, slightly lower than those of [N1114]HSO<sub>4</sub> and [Emim]HSO<sub>4</sub>. The conductivity of the three ILs is of the same order. In particular, the [Epdy]HSO<sub>4</sub> can provide higher performance than the [Emim]HSO<sub>4</sub>, even with a lower conductivity.

Fig. 3. Fuel cell stability test with [N1114]HSO<sub>4</sub> and [Emim]HSO<sub>4</sub>.Fig. 5. Conductivity of [N1114]HSO<sub>4</sub>, [Emim]HSO<sub>4</sub> and [Epdy]HSO<sub>4</sub> as a function of temperature.

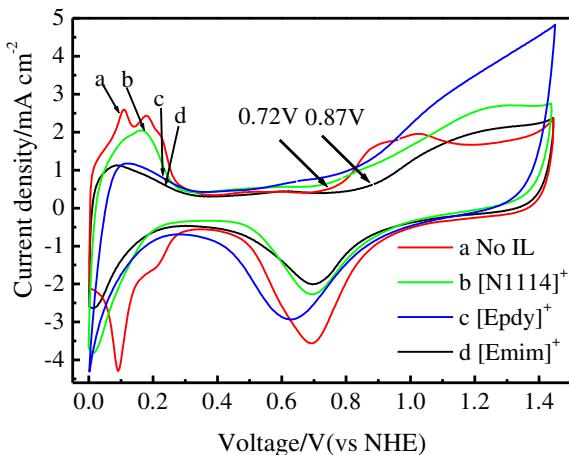


Fig. 6. Cyclic voltammogram for Pt/C in 0.5 M  $\text{H}_2\text{SO}_4$  with and without ionic liquids added at 25 °C, scan rate = 20 mV s<sup>-1</sup>.

Thus, the difference in fuel cell performance cannot be explained only by the ionic conductivity. The results also imply that the ionic conductivity is not of key importance for fuel cell performance with these electrolytes, although the high ionic conductivity has been emphasized by many reports [13,28].

### 3.3.2. CV tests

The Pt/C catalyst activity in the presence of the ILs was investigated, as the activity can be a possible factor influencing the fuel

cell performance. Until now, there have been limited reports on the effect of IL cations on the Pt/C catalyst although the influences of metal cations on the Pt catalyst have been investigated extensively [45–48]. The catalyst activity was studied using CV methods on the three ILs and the results are presented in Fig. 6.

As shown in Fig. 4, the EAS decreased dramatically when [Emim]  $\text{HSO}_4$  was added in the supporting electrolyte. The EAS dropped from  $70 \text{ m}^2 \text{ g}^{-1}$  for fresh Pt/C catalyst (line a) to  $20 \text{ m}^2 \text{ g}^{-1}$  when 10,000 ppm [Emim]  $\text{HSO}_4$  was added (line d) [29]. This decrease is believed to cause significant fuel cell performance decrease. The addition of [Epdy]  $\text{HSO}_4$  also caused a decrease in the EAS as shown by line c. However, the decrease was found to be less significant compared to that caused by the [Emim]  $\text{HSO}_4$ . The EAS was found to be approximately  $30 \text{ m}^2 \text{ g}^{-1}$  with 10,000 ppm [Epdy]  $\text{HSO}_4$  added, higher than that with the presence of [Emim]  $\text{HSO}_4$ . The change in EAS implies that the [Epdy]  $\text{HSO}_4$  has superior performance with Pt/C than [Emim]  $\text{HSO}_4$ . For [N1114]  $\text{HSO}_4$ , however, the EAS remains nearly unchanged when the IL concentration was 10,000 ppm. The results imply that [N1114]  $\text{HSO}_4$  has no significant negative influence on the EAS of the Pt/C catalyst.

In addition to the EAS decrease with the addition of [Emim]  $\text{HSO}_4$ , and [Epdy]  $\text{HSO}_4$ , the CV diagram shape was obviously changed in the  $\text{H}_{\text{upd}}$ -region. This change means severe suppression of the  $\text{H}_{\text{upd}}$ -region feature and catalyst activity. However, the shape change was less severe in the presence of [N1114]  $\text{HSO}_4$ . This also implies that the negative effect of [N1114]  $\text{HSO}_4$  was less severe than that from the [Emim]<sup>+</sup> or [Epdy]<sup>+</sup>.

Another important fact derived from Fig. 6 is that the potential for the Pt–OH formation gets more positive when [Emim]  $\text{HSO}_4$  is added. For the CV tests without ILs, the potential for the Pt–OH

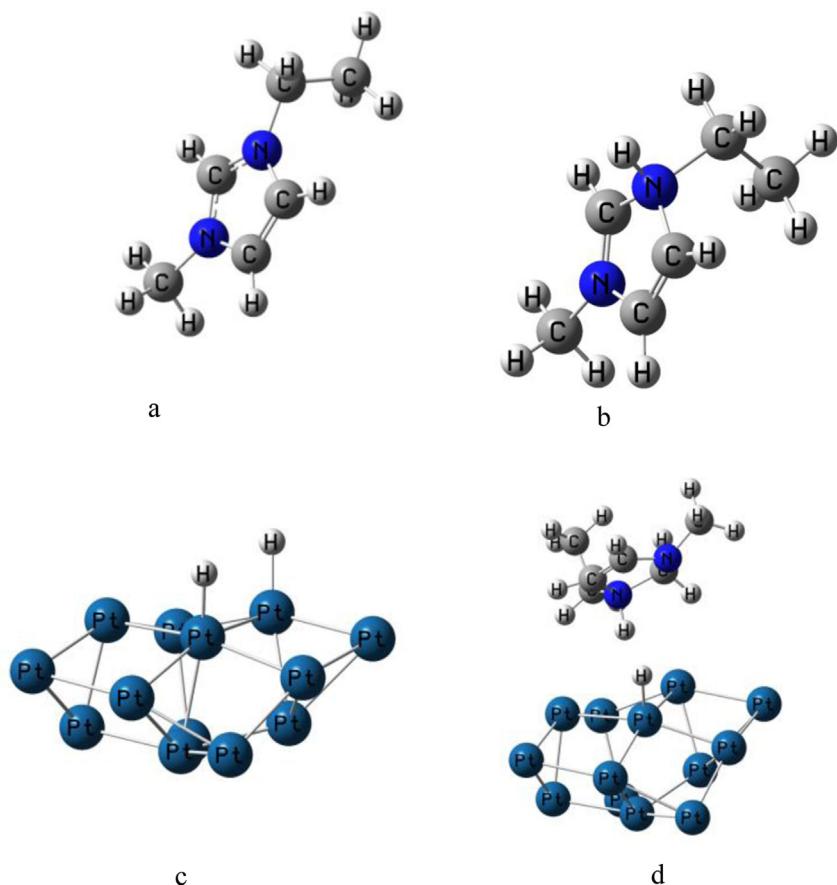


Fig. 7. Geometric structures of [Emim]<sup>+</sup> (a), protonated [Emim]<sup>+</sup> (b) protonated Pt13 cluster (c) and adsorption of protonated [Emim]<sup>+</sup> on protonated 3 cluster surface (d).

formation was found to be around 0.72 V [49]. However, when 10000 ppm [Emim]HSO<sub>4</sub> was added this potential increased 150 mV to 0.87 V. This increase implies that it becomes difficult for Pt–OH formation, which is believed to be the result of dissociative adsorption of molecular oxygen [49]. As a result, the increase means the dissociative adsorption of molecular oxygen on the Pt surface becomes increasingly difficult. The dissociative adsorption of oxygen is one of the important steps for ORR [49]. The increase in Pt–OH formation potential implies that it becomes difficult for the oxygen to be reduced by the Pt/C catalyst. As this reaction is a key electrode reaction for fuel cells, it is not surprising that the fuel cell performance should be impacted severely. This may explain why no significant elevation was observed in the fuel cell performance even after the negative effect of halide impurity was avoided for [Emim]HSO<sub>4</sub>, as can be observed in Section 3.2. However, this Pt–OH formation potential remains nearly the same or slightly decreased as 10,000 ppm [N1114]HSO<sub>4</sub> or [Epyd]HSO<sub>4</sub> was added. This means that the addition of the two ILs does not cause significant increase in the difficult for Pt–OH formation. Thus, the result also mean that the both the two non-imidazolium ILs has less negative impact than the [Emim]<sup>+</sup> does.

#### 3.4. Theoretical calculation

For a deeper understanding of the influence of these cations on the performance of Pt catalyst, a theoretical calculation has been performed to investigate the adsorption energy of these cations on Pt catalyst surface. [Emim]<sup>+</sup>, protonated [Emim]<sup>+</sup> and protonated Pt<sub>13</sub> cluster models are shown in Fig. 7(a)–(c), which is consistent with the experimental conditions. The calculated results show that the adsorption energy of protonated [Emim]<sup>+</sup> on protonated Pt<sub>13</sub> cluster surface is 57.3 Kcal mol<sup>-1</sup> (Fig. 5(d)), while that of [N1114]<sup>+</sup> and [Epyd]<sup>+</sup> is 1.8 and 48 kcal mol<sup>-1</sup>, respectively. This implies that more [Emim]<sup>+</sup> molecules will occupy the surface of Pt catalyst than [N1114]<sup>+</sup> or [Epyd]<sup>+</sup> does, and this will inhibit the catalytic performance of Pt catalyst since it is difficult to reach the substrate for the Pt catalyst. The proposed mechanism accounts well for experimental results shown in Figs. 2 and 6, in which the fuel cell performance with IL of [N1114]<sup>+</sup> is higher than that with imidazolium ILs. According to the works reported by the Hagiwara group [50,51], using pyrrolidinium cation (ethyl methyl pyrrolidinium, Epyo) as an electrolyte can provide performances higher than that with imidazolium ILs. The adsorption energy of pyrrolidinium cation on Pt catalyst surface was also calculated, which is 2.9 kcal mol<sup>-1</sup> and explains well why using pyrrolidinium cation as an electrolyte can provide performance higher than that with imidazolium ILs. Thus, the experiments and calculation of the present work suggest that the cation of the ILs used as an electrolyte has severe influence on fuel cell performance.

To make a clear comparison of the relationship between the fuel cell performance and cation, the ionic liquid, adsorption energy on Pt and the MPD of corresponding fuel cells were summarized in Table 2. It is clear that the larger the adsorption energy is, the lower the fuel cell performance. Thus, both the experiments and the data in the literature show that the fuel cell performance of PEMFC with IL as electrolyte is a strong function of the cations of the ILs.

**Table 2**

Summarized calculation and fuel cell test data for some common IL cations.

	[N1114] <sup>+</sup>	[Emim] <sup>+</sup>	[Epyd] <sup>+</sup>	[Epyo] <sup>+</sup>
AE/kcal mol <sup>-1</sup>	1.8	57.3	48	2.9
MPD/mW cm <sup>-2</sup>	65	1.6	15	35 [51]
Anion	HSO <sub>4</sub> <sup>-</sup>	HSO <sub>4</sub> <sup>-</sup>	HSO <sub>4</sub> <sup>-</sup>	(FH) <sub>n</sub> F

AE: calculated adsorption energy.

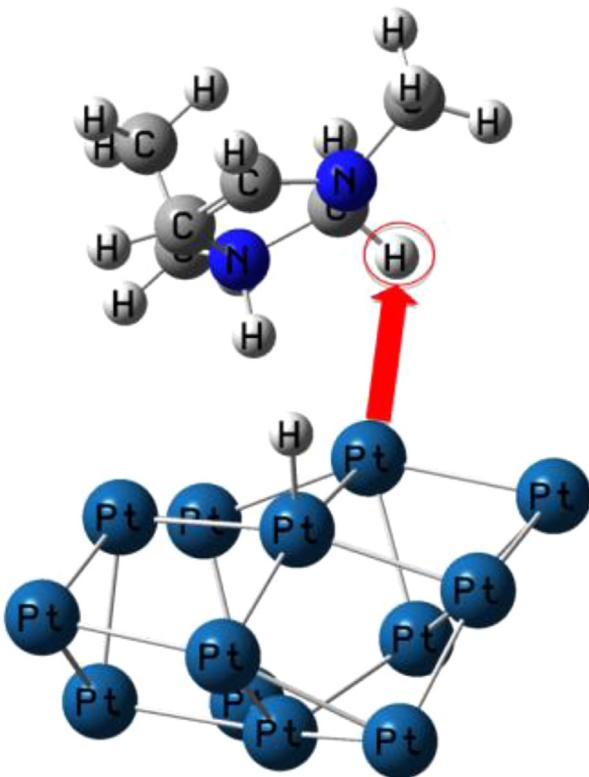


Fig. 8. The migration of proton form Pt to imidazole ring.

The calculation suggests that the proton adsorbed on the Pt surface may migrate to one carbon of the imidazolium ring under acid conditions as shown in Fig. 8. This may due to the cation structure. The C atom between two N atoms just connects three atoms (N, H and N), which prefers to bond to the fourth atom (Figs. 7(b) and 8). This results in the transfer of the Pt-bond proton to it.

#### 4. Conclusion

The impact of cation selection of ionic liquid on PEM fuel cell performance was studied, and a significant cation effect on catalyst performance was observed. A maximum power density of 65 mW cm<sup>-2</sup> with an IL of [N1114]HSO<sub>4</sub> as electrolyte was obtained while those for PEMFC with imidazolium ILs are mostly around 1 mW cm<sup>-2</sup>. This performance is the highest reported performance for PEMFC with ILs carried on an inert matrix. Subsequently, the reason for the performance elevation was investigated with experimental and theoretical methods. The results imply that the non-imidazolium ILs has less negative impact on the Pt/C catalyst. The theoretical calculation with Gaussian 03 program shows that the desorption energy of cations on the Pt catalyst varies with different cations. The results open a new door to elevate the performance of PEMFCs with ILs as electrolyte.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.jpowsour.2013.11.038>.

## References

- [1] J.S. Wilkes, *Green Chem.* 2 (2002) 73–80.
- [2] K.R. Seddon, A. Stark, M.J. Torres, *Pure Appl. Chem.* 12 (2000) 2275–2287.
- [3] M.n. Blesic, M. Swadzba-Kwasny, T. Belhocine, H.Q.N. Gunaratne, J.N.C. Lopes, M.F.C. Gomes, A.A.H. Padua, K.R. Seddon, L.P.N. Rebelo, *Phys. Chem. Chem. Phys.* 39 (2009) 8939–8948.
- [4] R.D. Rogers, K.R. Seddon, *Science* 5646 (2003) 792–793.
- [5] S.G. Liang, H.Z. Liu, Y.X. Zhou, T. Jiang, B.X. Han, *New J. Chem.* 11 (2010) 2534–2536.
- [6] B.C. Ranu, S. Banerjee, *Org. Lett.* 14 (2005) 3049–3052.
- [7] T.Y. Kim, W.J. Kim, S.H. Hong, J.E. Kim, K.S. Suh, *Angew. Chem. Int. Ed.* 21 (2009) 3806–3809.
- [8] R.F. de Souza, J.C. Padilha, R.S. Goncalves, J. Dupont, *Electrochim. Commun.* 8 (2003) 728–731.
- [9] U.A. Rana, M. Forsyth, D.R. MacFarlane, J.M. Pringle, *Electrochim. Acta* 0 (2012) 213–222.
- [10] M. Watanabe, H. Nakamoto, *Chem. Commun.* 24 (2007) 2539–2541.
- [11] H. Ye, J. Huang, J.J. Xu, N.K.A.C. Kodiweera, J.R.P. Jayakody, S.G. Greenbaum, *J. Power Sources* 2 (2008) 651–660.
- [12] M.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe, *Chem. Commun.* 8 (2003) 938–939.
- [13] H. Matsuoka, H. Nakamoto, M.A.B.H. Susan, M. Watanabe, *Electrochim. Acta* 19 (2005) 4015–4021.
- [14] H. Nakamoto, A. Noda, K. Hayamizu, S. Hayashi, H.O. Hamaguchi, M. Watanabe, *J. Phys. Chem. C* 3 (2007) 1541–1548.
- [15] V. Di Noto, E. Negro, J.Y. Sanchez, C. Iojou, *J. Am. Chem. Soc.* 7 (2010) 2183–2195.
- [16] S.Y. Lee, A. Ogawa, M. Kanno, H. Nakamoto, T. Yasuda, M. Watanabe, *J. Am. Chem. Soc.* 28 (2010) 9764–9773.
- [17] S.R. Narayanan, S.P. Yen, L. Liu, S.G. Greenbaum, *J. Phys. Chem. B* 9 (2006) 3942–3948.
- [18] N.V. Rees, R.G. Compton, *J. Solid State Electrochem.* 10 (2011) 2095–2100.
- [19] E. van de Ven, A. Chairuna, G. Merle, S.P. Benito, Z. Borneman, K. Nijmeijer, *J. Power Sources* (2013) 202–209.
- [20] Y.M. Kim, S.H. Choi, H.C. Lee, M.Z. Hong, K. Kim, H.I. Lee, *Electrochim. Acta* 26 (2004) 4787–4796.
- [21] J.Y. Feng, X.J. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, *Int. Eng. Chem. Res.* 10 (2003) 2058–2066.
- [22] Y. Zhiyong, D. Laub, M. Bensimon, J. Kiwi, *Inorg. Chim. Acta* 3 (2008) 589–594.
- [23] G.K.S. Prakash, F.A. Viva, O. Bretschger, B. Yang, M. El-Naggar, K. Nealson, *J. Power Sources* 1 111–117.
- [24] S. Holmberg, T. Lehtinen, J. Nasman, D. Ostrovskii, M. Paronen, R. Serimaa, F. Sundholm, G. Sundholm, L. Torell, M. Torkkel, *J. Mater. Chem.* 8 (1996) 1309–1317.
- [25] J. Gao, J. Liu, W. Liu, B. Li, Y. Xin, Y. Yin, Jungu, Z. Zou, *Int. J. Electrochem. Sci.* 12 (2011) 6115–6122.
- [26] S.S. Sekhon, P. Krishnan, B. Singh, K. Yamada, C.S. Kim, *Electrochim. Acta* 4 (2006) 1639–1644.
- [27] B.S. Lalia, K. Yamada, M.S. Hundal, J.S. Park, G.G. Park, W.Y. Lee, C.S. Kim, S.S. Sekhon, *Appl. Phys. A – Mater.* 3 (2009) 661–670.
- [28] Q.T. Che, R.H. He, J.S. Yang, L. Feng, R.F. Savinell, *Electrochim. Commun.* 5 (2010) 647–649.
- [29] J. Gao, J. Liu, W. Liu, B. Li, Y. Xin, Y. Yin, J. Gu, Z. Zou, *Int. J. Hydrogen Energy* 17 (2012) 13167–13177.
- [30] J. Kagimoto, K. Fukumoto, H. Ohno, *Chem. Commun.* 21 (2006) 2254–2256.
- [31] A.D. Becke, *J. Chem. Phys.* 7 (1993) 5648–5652.
- [32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, Gaussian 03, Revision E.01, 2004. Wallingford, CT.
- [33] G. Psolfogiannakis, A. St-Amant, M. Ternan, *J. Phys. Chem. B* 48 (2006) 24593–24605.
- [34] L. Xiong, Q. Zhao, H. Chen, Y. Wu, Z. Dong, Z. Zhou, F. Li, *Inorg. Chem.* 14 (2010) 6402–6408.
- [35] G. Scalmani, M.J. Frisch, *J. Chem. Phys.* 11 (2010) 114110–114114.
- [36] R.D. Rogers, *Nature* 7147 (2007) 917–918.
- [37] C.C. Cassol, G. Ebeling, B. Ferrera, J. Dupont, *Adv. Synth. Catal.* 1–2 (2006) 243–248.
- [38] M. Galinski, A. Lewandowski, I. Stepienak, *Electrochim. Acta* 26 (2006) 5567–5580.
- [39] H.L. Ngo, K. LeCompte, L. Hargens, A.B. McEwen, *Thermochim. Acta* 14 (2000) 97–102.
- [40] B.-E.M.a.l. Albinsson, *Ionics* 5–6 (1998) 415–421.
- [41] J.C. Padilha, J. Basso, L.G. da Trindade, E.M.A. Martini, M.O. de Souza, R.F. de Souza, *J. Power Sources* 19 (2010) 6483–6485.
- [42] S.S. Sekhon, B.S. Lalia, J.S. Park, C.S. Kim, K. Yamada, *J. Mater. Chem.* 23 (2006) 2256–2265.
- [43] V.R. Koch, L.A. Dominey, C. Nanjundiah, M.J. Ondrechen, *J. Electrochem. Soc.* 3 (1996) 798–803.
- [44] J.T.W. Wang, S.L.C. Hsu, *Electrochim. Acta* 7 (2011) 2842–2846.
- [45] S.A.S. Machado, A.A. Tanaka, E.R. Gonzalez, *Electrochim. Acta* 8 (1991) 1325–1331.
- [46] S.A.S. Machado, A.A. Tanaka, E.R. Gonzalez, *Electrochim. Acta* 17 (1994) 2591–2597.
- [47] S.A.S. Machado, A.A. Tanaka, E.R. Gonzalez, *Electrochim. Acta* 14 (1992) 2559–2564.
- [48] G. Kokkinidis, D. Sazou, I. Mountzis, *J. Electroanal. Chem. Interf. Electrochem.* 1 (1986) 135–147.
- [49] A.L. Wolf Vielstich, Hubert A. Gasteiger, *Handbook of Fuel Cells, Fundamentals Technology and Applications-cyclic Voltammetry*, Wiley & Sons, Inc., New York, 2003.
- [50] J.S. Lee, T. Nohira, R. Hagiwara, *J. Power Sources* 2 (2007) 535–539.
- [51] T.N. Pisis Kiatkittikul, Rika Hagiwara, *J. Power Sources* 220 (2012) 10–14.